

MODELLING ORGANIC SURFACES WITH SELF-ASSEMBLED MONOLAYERS

C. D. Bain and G. M. Whitesides*
Department of Chemistry
Harvard University
Cambridge MA 02138

Technical Report No. 20 (May 1989)

Interim Technical Report

(Accepted for publication in Angewandte Chemie)

DTIC
ELECTE
JUN 01 1989
S D C& D

DISTRIBUTION STATEMENT A
Approved for public release
Distribution Unlimited

PREPARED FOR DEFENSE ADVANCED RESEARCH PROJECTS AGENCY
1400 Wilson Boulevard
Arlington VA 22209

DEPARTMENT OF THE NAVY
Office of Naval Research, Code 1130P
800 North Quincy Street
Arlington VA 22217-5000

ARPA Order No.: NR 356-856
Contract No.: N00014-85-K-0898
Effective Date: 85 September 01
Expiration Date: 89 May 31

Principal Investigator: George M. Whitesides
(617) 495-9430

The views and conclusions in this document are those of the authors and should not be interpreted as necessarily representing the official policies, either expressed or implied, of the Defense Advanced Research Projects Agency or the U.S. Government.

89 5 30 161

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

| | | | |
|---|--------------------------------------|--|---------------------------|
| 1a. REPORT SECURITY CLASSIFICATION Unclassified | | 1b. RESTRICTIVE MARKINGS | |
| 2a. SECURITY CLASSIFICATION AUTHORITY | | 3. DISTRIBUTION / AVAILABILITY OF REPORT Approved for public release; distribution unlimited | |
| 2b. DECLASSIFICATION / DOWNGRADING SCHEDULE | | | |
| 4. PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report # 20 | | 5. MONITORING ORGANIZATION REPORT NUMBER(S) | |
| 6a. NAME OF PERFORMING ORGANIZATION Harvard University | 6b. OFFICE SYMBOL (if applicable) | 7a. NAME OF MONITORING ORGANIZATION Office of Naval Research | |
| 6c. ADDRESS (City, State, and ZIP Code) Office of Sponsored Research Holyoke Center, Fourth Floor Cambridge MA 02138-4993 | | 7b. ADDRESS (City, State, and ZIP Code) Code 1130P 800 North Quincy Street Arlington VA 22217-5000 | |
| 8a. NAME OF FUNDING / SPONSORING ORGANIZATION ONR/DARPA | 8b. OFFICE SYMBOL (if applicable) | 9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER | |
| 8c. ADDRESS (City, State, and ZIP Code) 800 North Quincy Street Arlington VA 22217-5000 | | 10. SOURCE OF FUNDING NUMBERS | |
| | | PROGRAM ELEMENT NO. 85-K-0898 | PROJECT NO. NR 356-856 |
| | | TASK NO. | WORK UNIT ACCESSION NO. |
| 11. TITLE (Include Security Classification) "Modelling Organic Surfaces with Self-Assembled Monolayers" | | | |
| 12. PERSONAL AUTHOR(S) Bain, C. D.; Whitesides, G. M. | | | |
| 13a. TYPE OF REPORT Interim | 13b. TIME COVERED FROM TO | 14. DATE OF REPORT (Year, Month, Day) May 1989 | 15. PAGE COUNT |
| 16. SUPPLEMENTARY NOTATION | | | |
| 17. COSATI CODES | | 18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) self-assembly, monolayers, thiols, gold, organic surfaces. (mgm) | |
| FIELD | GROUP SUB-GROUP | | |
| 19. ABSTRACT (Continue on reverse if necessary and identify by block number) The interfacial properties of organic materials are of critical importance in many applications, especially the control of wettability, adhesion, tribology, and corrosion. The relationships between the microscopic structure of an organic surface and its macroscopic physical properties are, however, only poorly understood. This short review presents a model system that has the ease of preparation and the structural definition required to provide a firm understanding of interfacial phenomena. Long-chain thiols, $\text{HS}(\text{CH}_2)_n\text{X}$, adsorb from <u>over</u> | | | |
| 20. DISTRIBUTION / AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS | | 21. ABSTRACT SECURITY CLASSIFICATION | |
| 22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. Joanne Milliken | | 22b. TELEPHONE (Include Area Code) | 22c. OFFICE SYMBOL |

19. ABSTRACT (Cont'd)

cont'd → solution onto gold and form densely packed, oriented monolayers. By varying the terminal functional group, X, of the thiol, organic surfaces can be created having a wide range of structures and properties. More complex systems can be constructed by coadsorbing two or more thiols with different terminal functional groups or with different chain lengths onto a common gold substrate. By these techniques, controlled degrees of disorder can be introduced into model surfaces. We have used these systems to explore the relationships between the microscopic structure of the monolayers (on a molecular and supramolecular scale) and their macroscopic properties. Wettability is a macroscopic interfacial property that has proved of particular interest.

Keyword:



| | |
|--------------------|-------------------------------------|
| Accession For | |
| NTIS CRA&I | <input checked="" type="checkbox"/> |
| DTIC TAB | <input type="checkbox"/> |
| Unannounced | <input type="checkbox"/> |
| Justification | |
| By | |
| Distribution / | |
| Availability Codes | |
| Dist | Avail and/or Special |
| A-1 | |

Modelling Organic Surfaces with Self-Assembled Monolayers[‡]

Colin D. Bain^{*†} and George M. Whitesides^{**†}

Abstract: The interfacial properties of organic materials are of critical importance in many applications, especially the control of wettability, adhesion, tribology, and corrosion. The relationships between the microscopic structure of an organic surface and its macroscopic physical properties are, however, only poorly understood. This short review presents a model system that has the ease of preparation and the structural definition required to provide a firm understanding of interfacial phenomena. Long-chain thiols, $\text{HS}(\text{CH}_2)_n\text{X}$, adsorb from solution onto gold and form densely packed, oriented monolayers. By varying the terminal functional group, X, of the thiol, organic surfaces can be created having a wide range of structures and properties. More complex systems can be constructed by coadsorbing two or more thiols with different terminal functional groups or with different chain lengths onto a common gold substrate. By these techniques, controlled degrees of disorder can be introduced into model surfaces. We have used these systems to explore the relationships between the microscopic structure of the monolayers (on a molecular and supramolecular scale) and their macroscopic properties. Wettability is a macroscopic interfacial property that has proved of particular interest.

[*] Dr. C. D. Bain

Department of Chemistry, University of Cambridge
Lensfield Road, Cambridge CB2 1EW (U.K.)

[**] Prof. G. M. Whitesides

Harvard University Chemical Laboratories
12 Oxford St., Cambridge MA 02138 (U.S.A.)

[†] Correspondence may be addressed to either author.

[§] This work was funded in part by the Office of Naval Research, by DARPA/URI, and by the National Science Foundation through grants to the Harvard University Materials Research Laboratory.

1. Introduction

Much of modern materials science has been devoted to the discovery, development and production of materials with desired combinations of bulk mechanical, electrical or optical properties. In an increasing number of materials systems, however, performance is determined not only by the properties of the bulk but also by the characteristics of interfaces either within the material or between the material and the outside world. Examples abound: the strength and toughness of a carbon fibre composite is strongly influenced by the bond between the fibre and the polymer matrix; cracks may propagate rapidly along grain boundaries; the biological response to implanted materials is critically determined by the properties of their surfaces; surface states can pin the Fermi level in semiconductors; water and oil repellency are determined by the outermost few angstroms of a material; optical losses occur through reflection, scattering and non-linear processes at interfaces. As trends towards miniaturisation continue, the ratio of surface to volume increases and the importance of understanding and controlling interfacial properties grows commensurately.

The goal of relating the microscopic (atomic, molecular and supramolecular) structure of a surface to its macroscopic physical, chemical or biological properties (wettability, corrosion resistance, adhesive strength, biocompatibility) is not trivial, and may prove as great a challenge as the development of new materials. Attaining this goal is made more difficult by the complexity and inaccessibility to study of many interfaces of practical importance. Consequently, the ability to create model surfaces in which the structure is controlled on an atomic scale plays a vital role. Epitaxial growth techniques, such as MBE and VPE, have provided a way forward in the study of semiconductors and ceramics, but such techniques cannot easily be applied to the synthesis of model organic surfaces. Recently it has become clear that organic monolayer films offer the level of structural control required for detailed studies of organic surfaces. Of all the types of monolayer film studied since Benjamin Franklin first poured oil onto Clapham Pond, two systems appear particularly promising: monolayers

prepared by adsorption of alkanethiols on gold,¹ silver, copper or platinum; and those generated by reaction of alkyltrichlorosilanes with silicon or glass.² In this review we will concentrate on monolayers of alkylsulphur compounds on gold, with the emphasis on our own research. First, we will discuss the difference between these self-assembled monolayers and films produced by the Langmuir-Blodgett (LB) technique. We will then summarise the structural properties of monolayers generated by adsorption of thiols on gold. The bulk of the review is devoted to explaining, with examples, how the structure of the monolayer-air or monolayer-liquid interface can be varied in a controlled manner, and to discussing the types of information that can be derived from studies of model organic surfaces.

2. Langmuir-Blodgett and Self-Assembled Monolayers

The traditional means of forming an organic monolayer film is to spread an insoluble molecule on an aqueous subphase, compress the film mechanically with a barrier until the molecules are densely packed and oriented approximately normal to the surface, and then to transfer this monolayer, if desired, to a solid substrate by "dipping" (Figure 1). Much elegant work has been performed using these Langmuir-Blodgett monolayers,³ and they remain an excellent class of materials when multilayers are desired. They do, however, suffer several drawbacks as model systems for studying interfacial properties. First, they are only metastable and tend to relax into more stable structural forms. Surface properties of LB-films are most easily studied after the film has been transferred to a solid substrate, a procedure that may be complicated by changes in the structure of the monolayer during the transfer process. Second, they are not normally chemically bonded to the substrate and hence are not robust. LB monolayers can often be removed from a substrate simply by rinsing with either aqueous or non-aqueous solvents. Third, one is restricted to molecules that form LB-films on water and that can be transferred intact to a substrate. It is, in particular, difficult to generate surfaces exposing polar functional groups at the monolayer-air interface by this technique. It is also

difficult to form highly crystalline monolayers since they tend to be brittle and crack easily upon compression or during transfer.

Self-assembled monolayers rely on a strong specific interaction between an adsorbate and a substrate to drive the spontaneous formation of a monolayer film (Figure 1).⁴ To prepare a self-assembled monolayer, the substrate is simply immersed in a dilute (~1 mM) solution of the adsorbate at room temperature for an interval varying from a few minutes to several days, depending on the system. The principal substrate in our studies has been a gold film (1000–2000 Å thick) evaporated onto a polished silicon wafer, and we have used long-chain organosulphur compounds, typically thiols, $\text{HS}(\text{CH}_2)_n\text{X}$, as adsorbates. The densely packed, oriented films that result are thermodynamically stable and mechanically robust. Monolayers of thiols on gold can be removed from the solutions from which they have been adsorbed and immersed in aqueous or non-aqueous solvents, in acid or in base, without apparent adverse effects. The range of organic species that can be incorporated into these monolayers is large: few ligands compete effectively with a thiol in coordinating to the gold, and the thiol group is sufficiently unreactive to be compatible with most other functional groups. A variety of chemical reactions can also be performed on the monolayers in order to interrogate the structure or to modify the surface. Self-assembled monolayers of thiols adsorbed on gold are thus well-suited for our studies.

We,⁵ and others,^{2,6} have also used alkyltrichlorosilanes as precursors to monolayers of alkylsiloxanes on glass or silicon. These monolayers exhibit greater thermal, chemical (except in the presence of aqueous base) and mechanical stability than thiols adsorbed on gold: they can even be heated in boiling water or scrubbed vigorously without degradation. The high reactivity of the SiCl_3 group limits the chemistry of surfaces that can be created directly by adsorption of alkyltrichlorosilanes on silicon. The thermal and chemical stability of the monolayers does, however, allow extensive synthetic modification of pre-formed films. Ulman,⁶ using a modification of a technique proposed by Sagiv,⁷ has recently demonstrated the feasibility of monolayer-by-monolayer synthesis of high-quality multilayer films using

alkyltrichlorosilanes. These multilayers have great potential for controlling the bulk optical and electrical properties of thin films, but are beyond the scope of this review.

3. Structure of Monolayers of Thiols on Gold

Our investigations have centred on the adsorption onto gold of linear thiols, $\text{HS}(\text{CH}_2)_n\text{X}$, where $n \geq 10$ and X is any one of a wide range of functional groups that are compatible with thiols and that do not disrupt the packing of the hydrocarbon chains. We and others have characterised the resulting films by a range of techniques including ellipsometry, TEM, contact angle, reflection adsorption infrared spectroscopy (RAIRS), X-ray photoelectron spectroscopy (XPS) and electrochemistry.⁸⁻¹³ The picture that emerges is of a pin-hole-free, monolayer film comprising a densely packed array of trans-extended hydrocarbon chains, strongly anchored to the gold surface through the sulphur atom, and tilted approximately 30° from the normal to the surface. The nature of the bonding between sulphur and gold has not yet been established incontrovertibly, but available evidence points to both alkanethiols and dialkyl disulphides generating gold thiolates (Au-SR) upon adsorption. (For clarity we will use terms such as "monolayer of alkanethiol" in this review to indicate the molecular precursor, even though the actual species on the surface is probably a thiolate.) The tail group, X, is the predominant chemical functionality exposed at the surface. The essential structure of the monolayer appears to be preserved for a number of tail groups exhibiting a range of intermolecular interactions.¹¹ Except for short chains ($n < 10$), the structure of the monolayer and the properties of the monolayer-liquid or monolayer-air interface appear to be largely independent of the length of the hydrocarbon chain.⁹

This last observation is significant. If we are to use monolayers of thiols on gold as models for other surfaces, or to study interfacial phenomena in general, it is important that the gold substrate and the sulphur-gold interface do not affect the measured properties at the monolayer-ambient interface. The gold does have an indirect effect on the properties of the

monolayer through its influence on the cant of the hydrocarbon chains and hence on the orientation of the tail group at the surface of the monolayer. (If the organic monolayer is very thin, the polarisability of the gold substrate will also influence the wetting of the surface.) Small changes in the orientation of functional groups at the surface can lead to measurable changes in interfacial properties. For example, the chain tilt of monolayers of thiols adsorbed on silver is approximately zero, compared with $\sim 30^\circ$ on gold; the contact angle of water on a monolayer terminated by hydroxyl groups on silver ($X = OH$) is 20° ,⁶ whereas on gold angles of $<15^\circ$ are observed. This residual influence of the substrate is not necessarily a disadvantage: the fact that we can even ask questions about the influence of the orientation of a functional group on the macroscopic properties of an interface is a testimony to the power of the technique of self-assembly.

4. Effect of the Chemical Structure of an Interface on Wettability

Wettability is a representative macroscopic physical property of surfaces that we have studied extensively. An understanding of the microscopic basis of wettability is important for two reasons: first, many technologies rely on controlling wettability; and second, the wettability of a flat surface is determined by interfacial free energies and hence reflects intermolecular interactions at the solid-liquid and solid-vapour interfaces.¹⁴ In fact, wettability appears to be an extremely sensitive analytical tool for elucidating the structure of surfaces. Wettability is quantified by the measurement of the contact angle, θ , between the tangent to a drop of liquid where it meets the surface and the surface itself. Different liquids probe different molecular forces. Water senses primarily polar functional groups in the substrate, whereas a hydrocarbon, such as hexadecane, interacts purely by dispersive forces. Different values of the contact angle may be observed for drop edges that have advanced or receded across the surface prior to measurement. Although this hysteresis in the contact angle undoubtedly carries

a wealth of structural information about the surface, no microscopic theory yet exists that explains the origin of hysteresis.

A large range of functional groups can be expressed at the surface of a monolayer of a thiol on gold. Thiols with highly polar tail groups, such as carboxylic acids, form monolayers that are wet by water and by all non-reactive organic liquids. Fluorinated thiols form monolayers that are more water and oil-repellent than Teflon. The hydrophobicity and oleophobicity of the surface can be varied almost independently between these two extremes (Table I). In general, the lower the surface tension, γ_v , of the probe liquid, the lower the contact angle. By judicious choice of tail group, this relationship can be reversed. For example, a monolayer of $\text{HS}(\text{CH}_2)\text{CO}_2\text{CH}_3$ is wet by acetonitrile ($\gamma_v = 29.3 \text{ mN/m}$; $\theta = 0^\circ$) but not by hexadecane ($\gamma_v = 27.2 \text{ mN/m}$; $\theta = 28^\circ$). We have, however, not yet succeeded in mimicking the unusual properties of the surface of water itself, which is wet by water (since any pure liquid wets itself) but not by hexadecane.

One of the key questions that we have sought to answer is how wettability is influenced by the depth of a species beneath the solid-liquid interface. The strength of the interaction between two bodies separated by a third medium can be calculated from bulk optical properties by Lifshitz theory. Given the short range of the intermolecular interactions that determine the wetting of organic surfaces, such continuum theories can at best provide only an approximate answer. Using monolayers we can tackle this problem from a molecular perspective.⁴ Figure 2 plots the contact angles of water and hexadecane on monolayers of ether-terminated alkanethiols, $\text{HS}(\text{CH}_2)_{16}\text{O}(\text{CH}_2)_n\text{CH}_3$, $n = 0-5$. In this study¹⁵ the polar ether group was buried progressively deeper beneath the monolayer-liquid interface by increasing the length of the terminal alkyl chain. The contact angles of hexadecane confirm that the dispersion interaction between the ether group and hexadecane is very short range, dropping to essentially zero when a 2-Å thickness of hydrocarbon material intervenes. Water was able to sense the polar ether group at greater depths beneath the monolayer-water interface: a butyl group was required to screen the ether oxygen fully from the supernatant drop. Similar results have been

obtained using amides in place of ethers.¹⁶ Thus we see that one only needs to control the structure of the outermost few angstroms of a smooth solid in order to determine its wetting properties. Furthermore, as an analytical technique, wettability approaches the best UHV spectroscopies in terms of surface sensitivity.

5. Construction of Complex Interfaces

5.1 Multiple Functional Groups

The ability to synthesise surfaces containing a unique functional group helps us to understand the contributions of individual chemical species to interfacial properties. Real surfaces, however, are complex both chemically and structurally. There is no *a priori* reason to assume that the different chemical components in an interface behave independently and hence that the properties of a multi-component surface can be inferred with confidence from the properties of surfaces composed of structured arrays of the pure components. The first step in extending our model to approximate real surfaces more closely is to introduce more than one functional group into the monolayer. To a certain extent this end can be achieved by performing reactions on the monolayer after formation. More generally, we can generate polyfunctional surfaces by coadsorbing two or more thiols on gold.

In interpreting coadsorption experiments, two questions immediately present themselves. First, does the composition of the monolayer reflect the relative concentrations of the two components in solution? Second, do the different components in the monolayer phase-segregate into macroscopic domains? The answer to both questions appears to be no. The composition of the monolayer is strongly influenced by interactions between the adsorbates and the solvent and among the tail groups within the monolayer. Changing the nature of the solvent, from ethanol to isooctane for example,¹ can dramatically alter the composition of a monolayer even when the concentrations in solution remain unchanged. If the adsorption components have different chain lengths, cohesive interactions between crystalline

hydrocarbon chains favour incorporation of the longer chain into the monolayer. Far from merely being an inconvenience, the relationships between the composition of the monolayer and the concentrations of the adsorbates provide a handle on the molecular interactions present in the monolayer, and offer valuable insights into other processes of self-assembly, such as membrane and micelle formation.

The question of the distribution of components within the monolayer is more difficult to resolve. Although numerous pieces of evidence militate against the formation of macroscopic islands (≥ 1000 Å across), the components are almost certainly not randomly dispersed, but form small clusters, as they do in solution, if by doing so the free energy is lowered. A better knowledge of the pair distribution function in these "mixed monolayers" would improve our understanding of real surfaces which, too, reconstruct to minimise their free energy.

A simple example of a mixed monolayer which displays the essential features of a coadsorption experiment is $\text{HS}(\text{CH}_2)_{11}\text{OH}/\text{HS}(\text{CH}_2)_{10}\text{CH}_3$ adsorbed from ethanol onto gold.¹⁷ Figure 3A displays the relationship between the mole fraction of $\text{HS}(\text{CH}_2)_{11}\text{OH}$ in the adsorption solution and in the monolayer. The compositions of the monolayers were determined from the intensity of the O(1s) peak obtained by XPS (Figure 3C). From solutions in ethanol there is a preference for adsorption of the methyl-terminated thiol. Adsorption of $\text{HS}(\text{CH}_2)_{11}\text{OH}$ is particularly disfavoured at low concentrations, possibly due to incomplete hydrogen-bonding of the terminal hydroxyl groups in the nonpolar environment provided by the surrounding methyl groups at the surface of the monolayer. The advancing contact angle of water is shown in Figure 3B as a function of the mole fraction, χ^{OH} , of the hydroxyl-terminated component in the monolayer. If the wettability of a mixed monolayer were simply a linear combination of the wetting properties of the constituent components, we would expect a linear relationship between $\cos \theta$ and χ^{OH} . The actual graph is concave: the hydroxyl groups at the surface of the monolayer are more hydrophilic at low χ^{OH} , when they are in a nonpolar environment, than at high χ^{OH} , when they are surrounded by other OH

groups to which they can hydrogen bond. This observation is consistent with the observed bias against adsorption of hydroxyl groups at low χ^{OH} .

Although mixed monolayers such as these may seem simple, the correlations between wettability and structure derived from such systems has proved invaluable in improving our understanding of a complex organic surface — chromic-acid-oxidised polyethylene — which contains a mixture of polar and nonpolar functionality.¹⁸ Comparison of the polymer with mixed monolayers supported the hypothesis that the polyethylene surface was composed of domains comprising largely polar or largely nonpolar groups, rather than containing a homogeneous distribution throughout the functionalised interphase.

The principles established for simple systems composed of two thiols are readily generalisable to cases in which both thiols are terminated by complex functional groups or in which there are more than two components in the monolayer.

5.2 Control over Surface Disorder

Many real surfaces differ from the model monolayers discussed so far in another important respect: they are disordered. The chains and tail groups in the densely packed, oriented monolayers presented above do not have the degrees of freedom available in an amorphous polymer or a fluid biological surface. As a consequence, the monolayer cannot reconstruct in response to changes in its environment, and we cannot easily use these monolayers to study dynamical processes at interfaces. We can introduce free volume, with the conformational freedom that entails, into the outer part of the monolayer by coadsorbing two thiols with different chain lengths.^{1,19,20} We expect the resulting mixed monolayers to have two distinct phases: the inner part, adjacent to the gold surface, remains densely packed (and hence insulates the monolayer-liquid or monolayer-air interface from the influence of the substrate), but the outer part of the monolayer contains fewer hydrocarbon chains per unit area and is free to become disordered (Figure 4). By placing functional groups at the ends of the

shorter chains, in the transition region between the ordered and disordered phases of the monolayer,²⁰ we can also introduce a degree of three-dimensionality beyond that achievable simply by varying the position of a functional group in a polymethylene chain.

The consequences of introducing disorder into the outer part of the monolayer can be seen clearly in monolayers composed of mixtures of $\text{HS}(\text{CH}_2)_{11}\text{OH}$ and $\text{HS}(\text{CH}_2)_{19}\text{OH}$ (Figure 5).¹⁹ Pure monolayers of either species expose only polar hydroxyl groups at the monolayer-liquid interface and hence yield very low contact angles with water ($\theta < 15^\circ$). In a mixed monolayer, however, the last eight carbons of the longer chains can form a disordered, liquid-like layer on top of the densely-packed lower phase of the monolayer. Since this disordered region exposes nonpolar polymethylene chains to the water drop, we expect to see a sharp increase in the contact angle (Figure 5). The observation of just such a maximum confirms our model and rules out the formation of large, single-component domains within the monolayer: each of these domains would expose only hydroxyl groups at the surface and hence the mixed monolayers would be wet by water, independent of composition. Comparison of the contact angles in Figure 5 with those shown in Figure 3 suggest that even the most disordered mixed monolayer still exposes an approximately 2:1 ratio of polar hydroxyl to nonpolar methylene groups to a water drop. This ratio is not unreasonable. We would expect the monolayer to reconstruct to maximise hydrogen-bonding and to minimise the number of hydrophobic contacts.

If the two thiols are terminated by methyl groups instead of hydroxyl groups, then the resulting mixed monolayers allow us to probe the effect of local structure on dispersive interactions and on the hydrophobic effect. Figure 6 shows the ellipsometric thickness, XPS intensities and contact angles for monolayers adsorbed from mixtures of $\text{HS}(\text{CH}_2)_{11}\text{CH}_3$ and $\text{HS}(\text{CH}_2)_{21}\text{CH}_3$ in isooctane. (The first two techniques serve to establish the composition of the monolayer.) Pure monolayers of either component expose a densely packed array of methyl groups at the surface of the monolayer, and are both hydrophobic and oleophobic. The surface of a monolayer containing an approximately equal mixture of the two components

resembles a liquid, linear hydrocarbon. The advancing contact angle of water is insensitive to the detailed structure of the hydrocarbon surface. On the other hand, hydrocarbon liquids, such as bicyclohexyl and hexadecane, show large changes in contact angle in response to variations in the structure of the surface. A corollary of these observations is that variations in the strength of the hydrophobic effect arise largely from hydrocarbon-hydrocarbon interactions rather than hydrocarbon-water interactions. There is also some evidence¹ that decane can penetrate into holes left in a monolayer of $\text{HS}(\text{CH}_2)_{21}\text{CH}_3$ by the presence of molecules of $\text{HS}(\text{CH}_2)_{11}\text{CH}_3$ — a primitive type of molecular recognition.

6. Concluding Remarks

We can only arrive at a detailed understanding of the complex physical and chemical properties of surfaces through the study of well-defined model systems. Phenomena such as wetting, adhesion, and friction are all functions (albeit complicated ones) of the microscopic chemical structure of a surface. Self-assembled monolayer films of thiols on gold are model systems in which the microscopic structural attributes of an organic surface can be varied independently and the influence on interfacial properties determined. We believe that they, and other related systems, will provide the bridge between the physical-organic chemistry of solutions and the materials science of organic solids. The research presented here is only a first step towards developing an understanding of organic surfaces. We still have to learn more about measuring and controlling the lateral distribution of functional groups. Many interesting features of wetting — especially the influence of roughness and chemical heterogeneity, and the origin of hysteresis — are still not understood. We have barely touched upon interfacial properties other than wetting, such as adhesion, friction and electrochemistry. Much remains to be learned about the physical-organic chemistry of condensed interphases.

Self-assembled monolayers are more than mere model systems for the surfaces of materials. They provide a starting point for practical technologies to solve interfacial problems. Two examples are the use of monolayers of alkylsiloxanes to promote adhesion or, with the opposite intent, to prevent catalyst particles from sticking to the walls of reactors. The intermolecular interactions controlling the structure of self-assembled monolayers are also acting in other spontaneously assembling systems. In studying them we will learn more about membranes, micelles and microemulsions.

Table I. Advancing Contact Angles of Water and Hexadecane on Monolayers of Representative Thiols on Gold.

(Insert sketch illustrating contact angle (sketch I))

| Thiol | θ_a | |
|---|------------------|----|
| | H ₂ O | HD |
| HS(CH ₂) ₂ (CF ₂) ₅ CF ₃ | 118 | 71 |
| HS(CH ₂) ₁₇ CH ₃ | 112 | 47 |
| HS(CH ₂) ₁₇ CH=CH ₂ | 107 | 39 |
| HS(CH ₂) ₁₉ Br ^a | 97 | <5 |
| HS(CH ₂) ₁₁ OCOCF ₃ ^d | 96 | 62 |
| HS(CH ₂) ₁₉ F ^a | 95 | <5 |
| HS(CH ₂) ₁₉ Cl ^a | 83 | <5 |
| HS(CH ₂) ₁₆ OCH ₃ | 75 | 41 |
| HS(CH ₂) ₁₀ CO ₂ CH ₃ | 67 | 28 |
| HS(CH ₂) ₁₁ CN ^b | 53 | <5 |
| HS(CH ₂) ₁₀ CONH ₂ ^c | 13 | <5 |
| HS(CH ₂) ₁₅ CO ₂ H | <10 | <5 |
| HS(CH ₂) ₁₁ OH | <10 | <5 |

From Ref. 1, except ^a B. Burbaum, unpublished results ^b P. Laibinis, unpublished result ^c L. Janes, unpublished result. ^d By reaction of a monolayer formed from $\text{HS}(\text{CH}_2)_{11}\text{OH}$ with trifluoroacetic anhydride.

Figure Captions

Fig. 1. A Langmuir-Blodgett monolayer (upper figure) can be transferred from the surface of water to a hydrophilic solid by raising the substrate through the water-air interface while maintaining a constant surface pressure with movable barriers. Self-assembled monolayers (lower figure) form spontaneously upon immersion of the substrate in a dilute solution of the adsorbate. Monolayer formation is driven by a strong, specific interaction between the head group (squares) and the surface of the substrate. One such system comprises thiols, RSH , adsorbed onto evaporated films of noble metals, such as gold, silver and copper. The cant (ϕ) of the hydrocarbon chains varies with the choice of substrate.

Fig. 2. ω -Mercaptoethers, $\text{HS}(\text{CH}_2)_{16}\text{O}(\text{CH}_2)_n\text{CH}_3$, adsorb from ethanol onto gold and form monolayers in which the depth of the polar ether group beneath the outer surface of the monolayer increases with increasing n . The advancing contact angles of water and hexadecane are shown as function of the length of the terminal alkyl chain. Also shown are the contact angles on polyethylene glycol (PEG) and on a monolayer of docosanethiol on gold, models of surfaces in which ether groups are, respectively, fully exposed to the contacting liquid, and completely buried.

Fig. 3. Monolayers exposing both methyl and hydroxyl groups at the surface of the monolayer may be formed by adsorption from solutions containing mixtures of $\text{HS}(\text{CH}_2)_{11}\text{OH}$ and $\text{HS}(\text{CH}_2)_{10}\text{CH}_3$. Fig. 3A plots the mole fraction of the hydroxyl-terminated chain in the monolayer as a function of the mole fraction in solution. For clarity, the calculation of the mole fraction in solution included only the thiol species. Fig. 3B shows the advancing contact angles of water as a function of the composition of the monolayer. Fig. 3C shows the oxygen (1s) region of the XPS spectra of the monolayers. The areas under these peaks were used to calculate the compositions of the monolayers.

Fig. 4. Schematic illustration of monolayers of hydroxyl-terminated thiols on gold. (A) Pure monolayer of $\text{HS}(\text{CH}_2)_{19}\text{OH}$; (B) monolayer containing equal amounts of $\text{HS}(\text{CH}_2)_{19}\text{OH}$ and $\text{HS}(\text{CH}_2)_{11}\text{OH}$. The inner part of the monolayer is densely packed, the outer part loosely packed and disordered; (C) pure monolayer of $\text{HS}(\text{CH}_2)_{11}\text{OH}$.

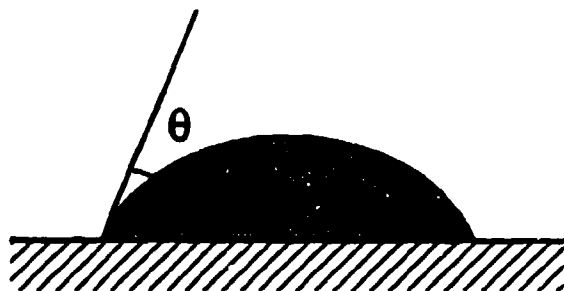
Fig. 5. Ellipsometric thickness and advancing contact angles of water for mixed monolayers of $\text{HS}(\text{CH}_2)_{19}\text{OH}$ and $\text{HS}(\text{CH}_2)_{11}\text{OH}$. The abscissa represents the ratio of concentrations of $\text{HS}(\text{CH}_2)_{19}\text{OH}$ to $\text{HS}(\text{CH}_2)_{11}\text{OH}$ in solution. The maximum in contact angle correlates approximately with the monolayer shown schematically in Fig. 4B.

Fig. 6. Mixed monolayers formed by coadsorption of $\text{HS}(\text{CH}_2)_{21}\text{CH}_3$ and $\text{HS}(\text{CH}_2)_{11}\text{CH}_3$ from isooctane. The abscissa represents the ratio of concentrations of $\text{HS}(\text{CH}_2)_{21}\text{CH}_3$ to $\text{HS}(\text{CH}_2)_{11}\text{CH}_3$ in solution. Fig. 6A plots the ellipsometric thickness of the monolayers. Fig. 6B plots the intensity of the $\text{C}(1s)$ and $\text{Au}(4f_{7/2})$ peaks obtained by XPS. The compositions of the monolayers can be calculated from the intensities of these peaks. Fig. 6C shows the advancing contact angles of water, hexadecane and bicyclohexyl.

References

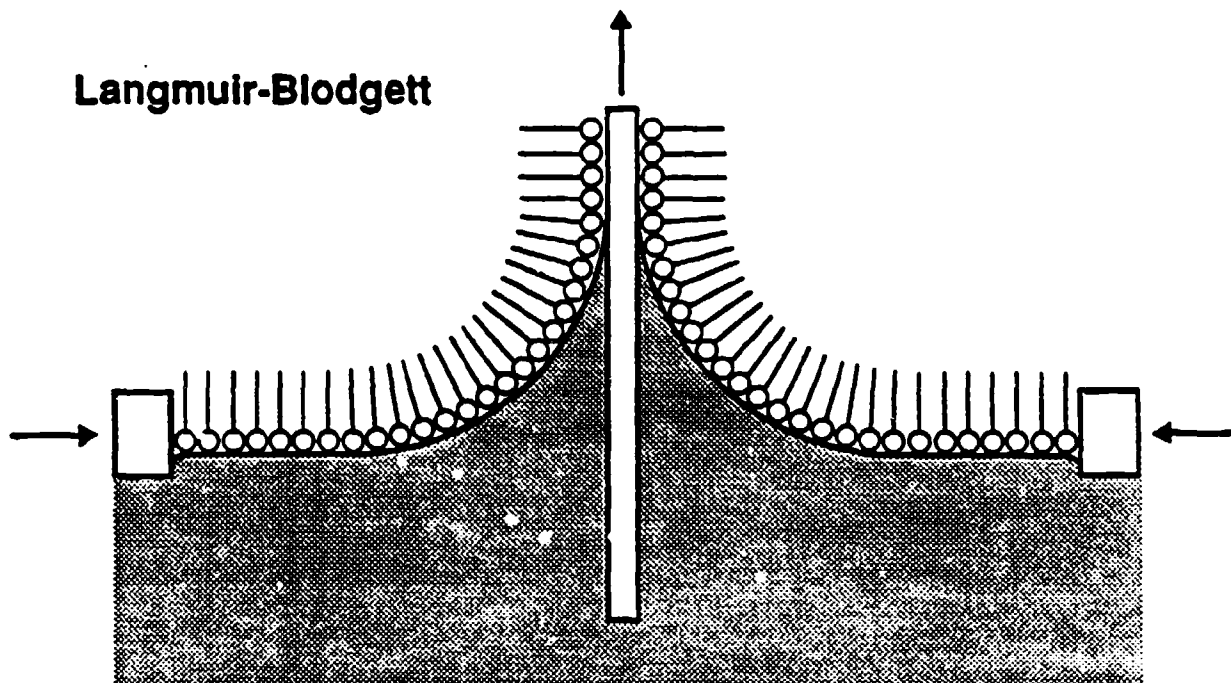
- ¹ C. D. Bain, PhD Thesis, Harvard 1988. G. S. Ferguson, G. M. Whitesides, *Chemtracts* 1 (1988) 171.
- ² J. Sagiv, *J. Am. Chem. Soc.* 102 (1980) 92.
- ³ See, for example, a recent review in *Advanced Materials*: H. Möhwald, *Angew. Chem.* 100 (1988) 750.
- ⁴ For a review of early work on self-assembled monolayers, see W. A. Zisman in F. M. Fowkes (Ed.): *Contact Angles, Wettability, and Adhesion*, Advances in Chemistry 43, American Chemical Society, Washington, DC 1964, pp 1-51.
- ⁵ S. R. Wasserman, G. M. Whitesides, I. M. Tidswell, B. M. Ocko, P. S. Pershan, J. D. Axe, *J. Am. Chem. Soc.*, in press; S. Wasserman, Y.-T. Tao, G. M. Whitesides, *Langmuir*, in press.
- ⁶ N. Tillman, A. Ulman, T. L. Penner, *Langmuir*, in press.
- ⁷ L. Netzer, R. Iscovici, J. Sagiv, *Thin Solid Films* 99 (1982) 235.
- ⁸ R. G. Nuzzo, D. L. Allara, *J. Am. Chem. Soc.* 105 (1983) 4481.
- ⁹ C. D. Bain, E. B. Troughton, Y.-T. Tao, J. Evall, G. M. Whitesides, R. G. Nuzzo, *J. Am. Chem. Soc.* 111 (1989), 321.ze
- ¹⁰ M. D. Porter, T. B. Bright, D. L. Allara, C. E. D. Chidsey, *J. Am. Chem. Soc.* 109 (1987) 3559.
- ¹¹ R. G. Nuzzo, L. H. Dubois, D. L. Allara, submitted for publication in *J. Am. Chem. Soc.*
- ¹² L. Strong, G. M. Whitesides, *Langmuir* 4 (1988) 546.
- ¹³ C. D. Bain, G. M. Whitesides, *J. Phys. Chem.*, in press.
- ¹⁴ P. G. DeGennes, *Rev. Mod. Phys.* 57 (1985) 827; J. N. Israelachvili: *Intermolecular and Surface Forces*, Academic Press, London 1985.
- ¹⁵ C. D. Bain, G. M. Whitesides, *J. Am. Chem. Soc.* 110 (1988) 5897.
- ¹⁶ B. Burbaum, L. Janes, G. M. Whitesides, unpublished results.
- ¹⁷ C. D. Bain, G. M. Whitesides, *J. Am. Chem. Soc.* 110 (1988) 6560.

- 18 S. R. Holmes-Farley, C. D. Bain, G. M. Whitesides, *Langmuir* 4 (1988) 921.
- 19 C. D. Bain, G. M. Whitesides, *Science (Washington, D.C.)* 240 (1988) 62.
- 20 C. D. Bain, G. M. Whitesides, *J. Am. Chem. Soc.* 110 (1988) 3665.



SKETCH :

Langmuir-Blodgett



Self-Assembled

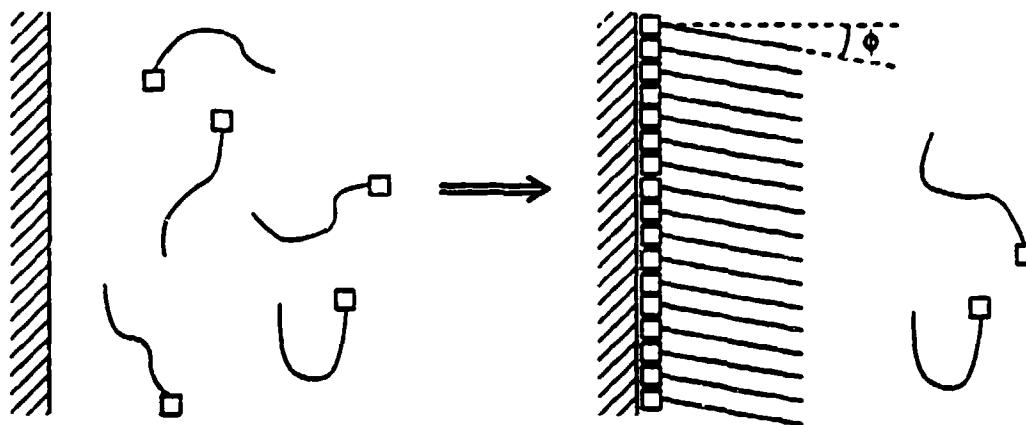


FIGURE 1

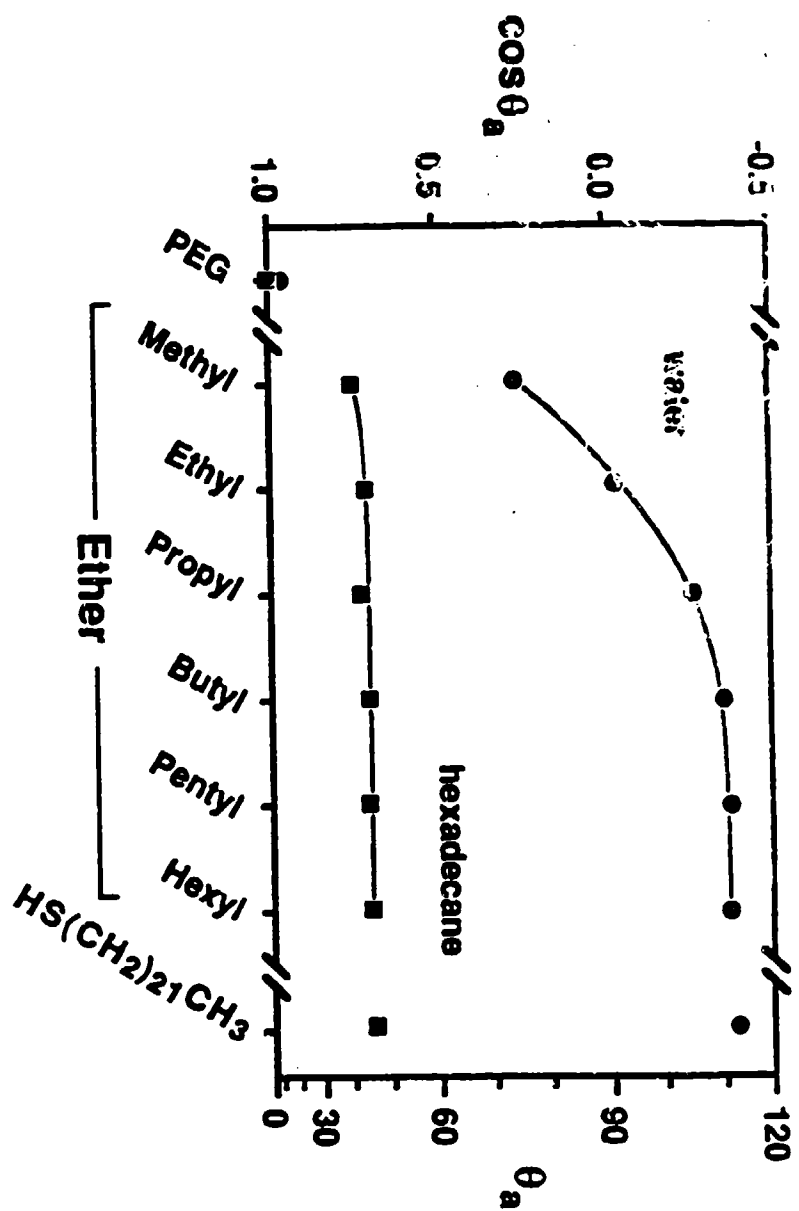


FIGURE 7

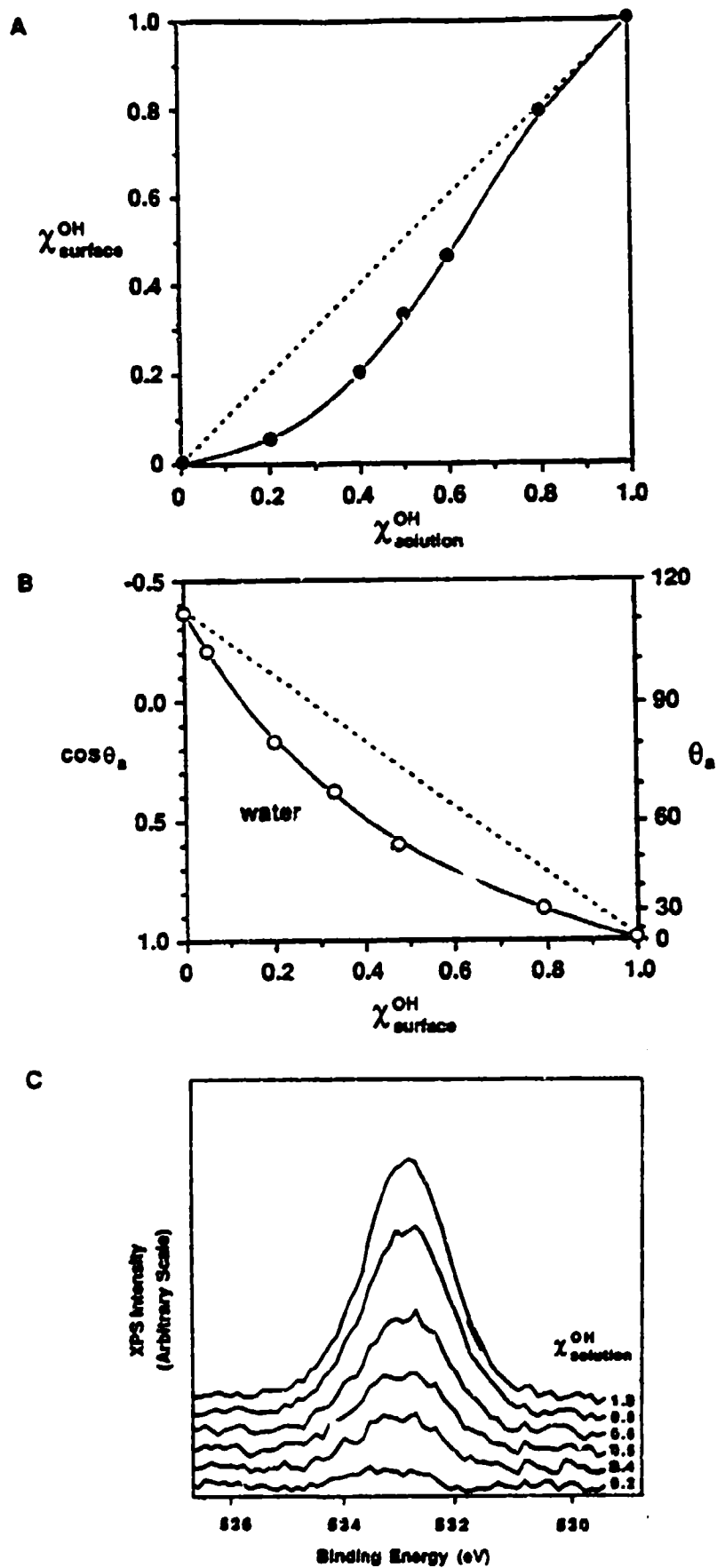


FIGURE 3

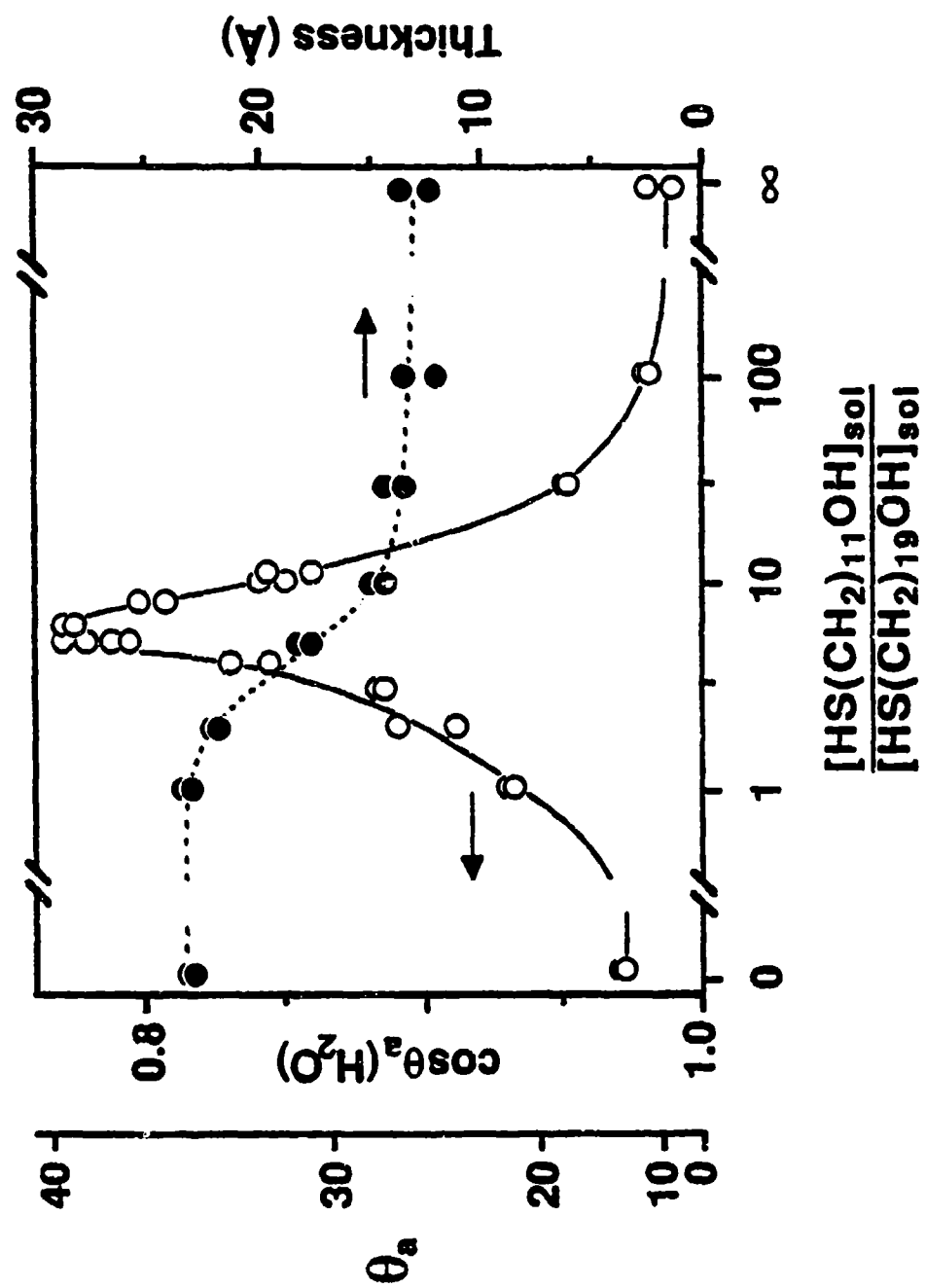
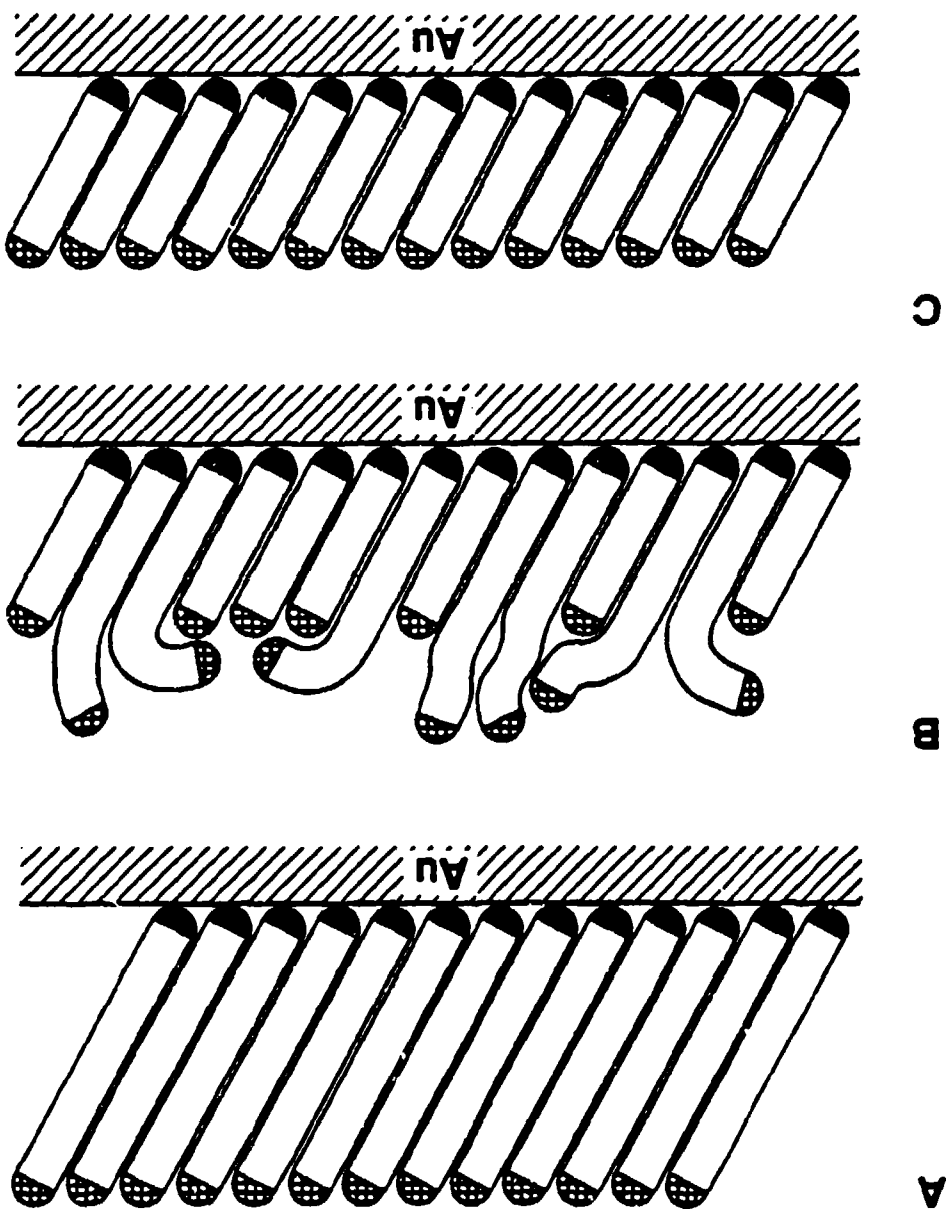


Figure 5



Key

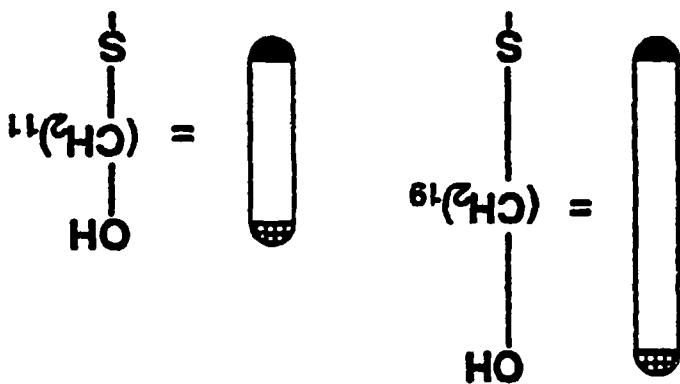


FIGURE 1

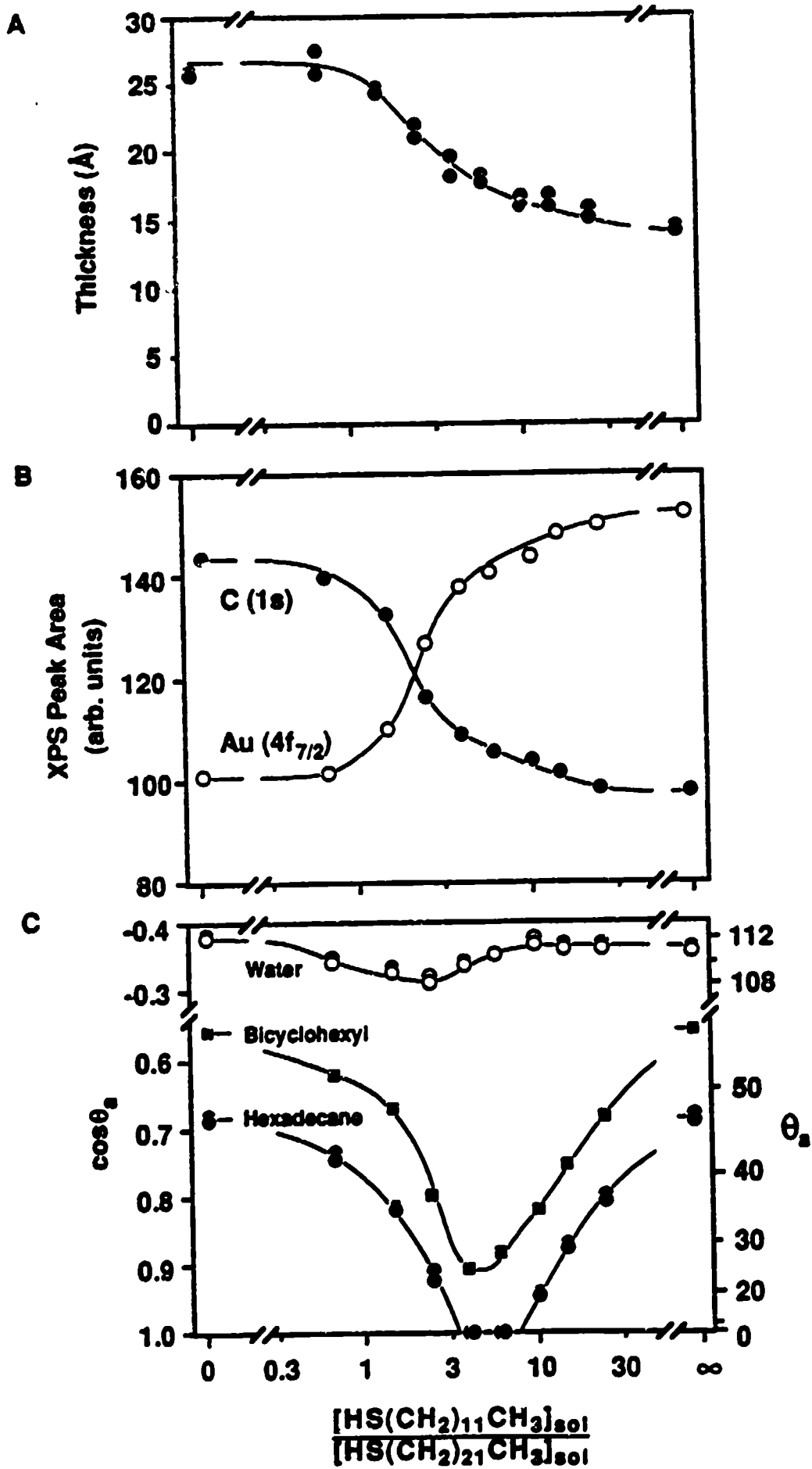


FIGURE 6

TECHNICAL REPORT DISTRIBUTION LIST, GENERAL

| | <u>No. Copies</u> | | <u>No. Copies</u> |
|--|------------------------------|--|-----------------------|
| Office of Naval Research Chemistry Division, Code 1113 800 North Quincy Street Arlington, VA 22217-5000 | 3 | Dr. Ronald L. Atkins Chemistry Division (Code 385) Naval Weapons Center China Lake, CA 93555-6001 | 1 |
| Commanding Officer Naval Weapons Support Center Attn: Dr. Bernard E. Douda Crane, IN 47522-5050 | 1 | Chief of Naval Research Special Assistant for Marine Corps Matters Code OOMC 800 North Quincy Street Arlington, VA 22217-5000 | 1 |
| Dr. Richard W. Drisko Naval Civil Engineering Laboratory Code L52 Port Hueneme, California 93043 | 1 | Dr. Bernadette Eichinger Naval Ship Systems Engineering Station Code 053 Philadelphia Naval Base Philadelphia, PA 19112 | 1 |
| Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314 | 2 <u>high quality</u> | Dr. Sachio Yamamoto Naval Ocean Systems Center Code 52 San Diego, CA 92152-5000 | 1 |
| David Taylor Research Center Dr. Eugene C. Fischer Annapolis, MD 21402-5067 | 1 | David Taylor Research Center Dr. Harold H. Singerman Annapolis, MD 21402-5067 ATTN: Code 283 | 1 |
| Dr. James S. Murday Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375-5000 | 1 | | |

POLYMER PROGRAM DISTRIBUTION LIST

Dr. J. M. Augl
Naval Surface Weapons Center
White Oak, MD 20910

Dr. A. S. Abhiraman
School of Chemical Engineering
Georgia Institute of Technology
Atlanta, GA 30332

4132033

Dr. Harry R. Allcock
Department of Chemistry
Pennsylvania State University
University Park, PA 16802

Dr. Chris W. Allen
Department of Chemistry
University of Vermont
Burlington, VT 05405

4132007

413c012

Dr. Ronald D. Archer
Department of Chemistry
University of Massachusetts
Amherst, MA 01003

Dr. Ali S. Argon
Mechanical Engineering Department
Massachusetts Institute of Technology
Cambridge, MA 02139

413c028

a400005df

Dr. William J. Bailey
Department of Chemistry
University of Maryland
College Park, MD 20742

Dr. Kurt Baum
Fluorochem, Inc.
680 S. Ayon Avenue
Azusa, CA 91702

413a006

4000021sbi

Dr. Frank D. Blum
Department of Chemistry
University of Missouri - Rolla
Rolla, MO 65401

Dr. Len J. Buckley
Naval Air Development Center
Code 6063
Warminster, PA 18974

413m005

Dr. F. James Boerio
Materials Science & Engineering Dept.
University of Cincinnati
Cincinnati, Ohio 45221

Dr. Ivan Caplan
DTNSRDC Annapolis
Code 0125
Annapolis, MD 21401

413m012

Dr. Robert E. Cohen
Department of Chemical Engineering
Massachusetts Institute of Technology
Cambridge, MA 02139

4132001

Dr. E. Fischer
DTNSRDC Code 2853
Annapolis, MD 21402

Dr. Curtis W. Frank
Department of Chemical Engineering
Stanford University
Stanford, CA 94305

413h005

Dr. Gregory S. Girolami
School of Chemical Sciences
University of Illinois
Urbana-Champaign, IL 61801

4132014

Dr. Robert H. Grubbs
Department of Chemistry
California Institute of Technology
Pasadena, CA 91124

4132019

Dr. James F. Haw
Department of Chemistry
Texas A&M University
College Station, TX 77843

413c039

Dr. Stuart L. Cooper
Department of Chemical Engineering
University of Wisconsin
Madison, WI 53706

4132006

Dr. Warren T. Ford
Department of Chemistry
Oklahoma State University
Stillwater, OK 74078

413h006

Dr. John K. Gillham
Department of Chemical Engineering
Princeton University
Princeton, New Jersey 08544

413c005

Dr. Bernard Gordon
Department of Polymer Science
Pennsylvania State University
University Park, PA 16802

413c025

Dr. Henry K. Hall
Department of Chemistry
University of Arizona
Tucson, AZ 85721

413j009

Dr. Alan J. Heeger
Department of Physics
University of California, Santa Barbara
Santa Barbara, CA 93106

4132012

Dr. Pat J. Hendra
Department of Chemistry
University of Southampton
Highfield Southampton 509 5NH
United Kingdom
4134001

Dr. Bruce S. Hudson
Department of Chemistry
University of Oregon
Eugene, Oregon 97403

413c018

Dr. Hatsu Ishida
Department of Macromolecular Science
Case Western Reserve University
Cleveland, OH 44106

413m008

Dr. Paul M. Lahti
Department of Chemistry
University of Massachusetts
Amherst, MA 01003

413c037

Dr. Robert W. Lenz
Polymer Science and Engineering Dept.
University of Massachusetts
Amherst, MA 01002

441c013

Dr. Alan D. MacDiarmid
Department of Chemistry
University of Pennsylvania
Philadelphia, PA 19104

a400004df

Dr. Charles E. Hoyle
Department of Polymer Science
University of Southern Mississippi
Hattiesburg, MS 39406-0076

413c026

Dr. Leonard V. Interrante
Department of Chemistry
Rensselaer Polytechnic Institute
Troy, NY 12181

413c014

Dr. Jeffrey T. Koberstein
Institute of Materials Science
University of Connecticut
Storrs, CT 06268

4132013

Dr. Richard M. Laine
Washington Technology Center
University of Washington
Seattle, WA 98195

s400033srh

Dr. Geoffrey Lindsay
Chemistry Division - Code 087
Naval Weapons Center
China Lake, CA 93555

4132036

Dr. Chris W. Macosko
Materials Science & Engineering Dept.
University of Minnesota
Minneapolis, MN 55455

4132029

Dr. Joseph H. Magill
Materials Science & Engineering Dept.
University of Pittsburgh
Pittsburgh, PA 15161

413c013

Dr. Tobin J. Marks
Department of Chemistry
Northwestern University
Evanston, IL 60201

413c030

Dr. Krzysztof Matyjaszewski
Department of Chemistry
Carnegie Mellon University
Pittsburgh, PA 15213

413j002

Dr. William B. Moniz
Code 6120
Naval Research Laboratory
Washington, DC 20375-5000

4132012

Dr. Virgil Percec
Department of Macromolecular Science
Case Western Reserve University
Cleveland, OH 44106-2699

413c024

Dr. Roger S. Porter
Dept. of Polymer Science & Engineering
University of Massachusetts
Amherst, MA 01002

413m006

Dr. Leo Mandelkern
Department of Chemistry
Florida State University
Tallahassee, FL 32306-3015

4132018

Dr. Lon J. Mathias
Department of Polymer Science
University of Southern Mississippi
Hattiesburg, MS 30406-0076

413m003

Dr. James E. McGrath
Department of Chemistry
Virginia Polytechnic Institute
Blacksburg, VA 24061

4132007

Dr. Kay L. Paciorek
Ultrasystems Defense and Space, Inc.
16775 Von Karman Avenue
Irvine, CA 92714

s400029srh

Dr. Martin Pomerantz
Department of Chemistry
University of Texas at Arlington
Box 19065
Arlington, TX 76019-0065
a400008df

Dr. T. J. Reinhart, Jr.
Nonmetallic Materials Division
Air Force Materials Laboratory (AFSC)
Wright-Patterson AFB, OH 45433

Dr. Arnost Reiser
Institute of Imaging Sciences
Polytechnic University
333 Jay Street
Brooklyn, NY 11021

4132022

Dr. Charles M. Roland
Code 6120
Naval Research Laboratory
Washington, DC 20375-5000

413m009

Dr. Ronald Salovey
Department of Chemical Engineering
University of Southern California
Los Angeles, CA 90089

413m010

Dr. Jerry I. Scheinbeim
Dept. of Mechanics & Materials Science
Rutgers University
Piscataway, NJ 08854

4132009

Dr. L. E. Slotter
Code Air 931-A
Naval Air Systems Command
Washington, D. C. 20361-9310

Dr. Dietmar Seyferth
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, MA 02139

413c004

Dr. Ferdinand Rodriguez
Department of Chemical Engineering
Cornell University
Ithaca, NY 14853

413c011

Dr. Michael F. Rubner
Materials Science & Engineering Dept.
Massachusetts Institute of Technology
Cambridge, MA 02139

413m007

Dr. Jacob Schaefer
Department of Chemistry
Washington University
St. Louis, MO 63130

413m001

Dr. Lawrence R. Sita
Department of Chemistry
Carnegie Mellon University
Pittsburgh, PA 15213

4132030

Dr. Richard R. Schrock
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, MA 02139

4132038

Dr. David S. Soane
Department of Chemical Engineering
University of California, Berkeley
Berkeley, CA 94720-9989

413h004

Dr. Les H. Sperling
Materials Research Center #32
Lehigh University
Bethlehem, PA 18015

413c002

Dr. C. S. Sung
Institute of Materials Science
University of Connecticut
Storrs, CT 06268

413m011

Dr. C. H. Wang
Department of Chemistry
University of Utah
Salt Lake City, Utah 84112

413c020

Dr. Robert A. Weiss
Department of Chemical Engineering
University of Connecticut
Storrs, CT 06268

a400006df

Dr. Garth L. Wilkes
Department of Chemical Engineering
Virginia Polytechnic Institute
Blacksburg, VA 24061

4132020

Dr. Richard S. Stein
Polymer Research Institute
University of Massachusetts
Amherst, MA 01002

4132008

Dr. Sukant K. Tripathy
Department of Chemistry
University of Lowell
Lowell, MA 01854

4132016

Dr. Kenneth B. Wagener
Department of Chemistry
University of Florida
Gainesville, FL 32611

a400007df

Dr. George M. Whitesides
Department of Chemistry
Harvard University
Cambridge, MA 02138

4132010